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RELATIVISTIC SELF-CONSISTENT FIELD STUDIES OF ATOMS AND MOLECULES

FINAL REPORT

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RELATIVISTIC SCF AND MANY-BODY STUDIES OF ATOMS AND MOLECULES

Dirac-Fock balanced Gaussian basis method that employs an extended nucleus model has been implemented, and applied to a number of atoms and the hydrogen molecular ion. The balanced expansion method does not introduce any of the variational instabilities that have plagued the early Dirac-Fock basis expansion calculations. Relativistic diagrammatic perturbation theory method has been developed and applied to a number of atoms in order to simultaneously take into account both relativistic and correlation effects. These studies showed that the Dirac-Fock balanced Gaussian basis expansion and the relativistic many-body methods are capable of providing accurate Dirac-Fock and correlation energies.

SUMMARY

Dirac-Fock SCF calculations by the method of expansion in a basis have been plagued by appearance of spurious solutions, and by the so-called "variational collapse", a phenomenon in which computed energies lie below the numerical limits. These are associated with problems of insuring that basis sets for the large and small components of the Dirac spinor are properly balanced, and of insuring that the wave function behaves properly near the nucleus[1]. The lack of an expansion scheme capable of guaranteeing an upperbound to the true energy has proven to be the major barrier to the practical application of basis set Dirac-Fock SCF to atoms and molecules.

Identification of the sources of the difficulties has allowed us to develop an expansion method, the Dirac-Fock balanced Gaussian basis expansion that employs the finite nucleus model [1,3-5,7]. In the "balanced" Gaussian basis expansion, the basis sets for the large and small components are chosen such that they produce the correct result in the limit as the speed of light tends to infinity, and such that, at finite speed of light, they make the correct approach to the boundary at the nucleus. We have implemented the Dirac-Fock method that employs the finite nucleus model, and applied to a series of atoms up to mercury[13] and to hydrogen molecular ion[4,5]. These calculations have shown that the Gaussian basis expansion method is competitive in computational speed and accuracy with numerical finite-difference treatments.

Dirac-Fock wave functions have the advantage that they provide results which may be directly compared to those obtained with the most popular non-relativistic method, the Hartree-Fock method. But accurate treatment of atomic and molecular systems makes it necessary to refine the Dirac-Fock treatments to include finer relativistic effects as well as the effects of electron correlation. To this end, we have developed a relativistic many-body perturbation method which simultaneously take into account both relativistic and correlation effects[10,12]. The calculations employ diagrammatic perturbation theory with single configuration Dirac-Fock ground state reference wave functions.

A computer program for the relativistic many-body perturbation theory calculations has been developed, and applied to systems up to the Ar atom in order to study the effects of relativity and the electron correlation on the electronic structure of atoms.

* See List of Publications.

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LIST OF PERSONNEL AND ADVANCED DEGREES EARNED

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- 2) W. Rodriguez, Chemical Physics Program, UPR, Rio Piedras
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